RELATION BETWEEN THE PROFILE AND THE MECHANICAL STRENGTH OF AN INTERFACE BETWEEN TWO POLYMERS.

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The understanding of the mechanical resistance of an interface between two polymers is very important for the control of adhesion, fracture and interfaces/ interphases in composites polymer systems. Industrial applications are numerous. Here we focus on elastomers, which are often present in these systems. We are interested in the relation between :

- the profile of an interface created between two polymer layers. If one layer is made of perdeuterated polymer, and the second of non-perdeuterated polymer, neutron reflectivity gives access to this profile on the 10 Å to 100 Å scale ;
- and the mechanical strength of such an interface, measured using the razor blade test (from 2 to 300 J/m^2).

We have considered the three cases where none of the layers, one or both are cross-linked. The chains are always polystyrene. In the absence of cross-linking, we have a polymer melt, which is liquid above the glass transition Tg.=100°C. With cross-linking we have a statistical network, where the cross-links are distributed at random. We characterize it by the average number of units between two successive cross-links, **N**, obtained from chemical titration.

Making the sample (Figure 1).
The samples for the two methods have been done in order to get interfaces as similar as possible.

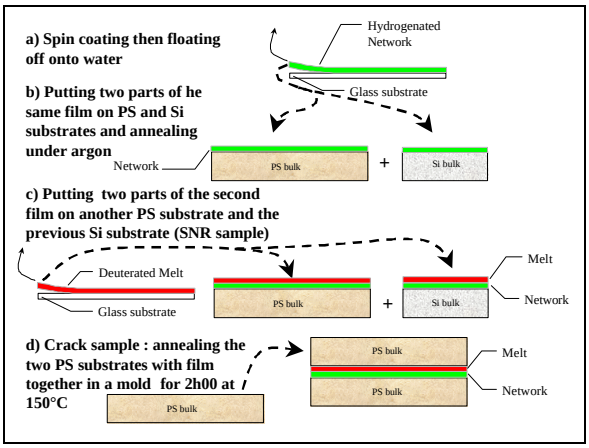

Figure 1. Making the sample

The layers, with thickness of several thousands Å, are made by spin coating on glass a polystyrene solution, or from aminomethylated polystyrene, which is chemically cross-linked during and after the drying process (Figure 1a). Each layer is removed from the glass by immersion into water (floating). We divide it in two halves (Figure 1b).
For neutron reflectivity, one deuterated half is deposited onto a Silicon wafer, annealed, then a non perdeuterated half is floated on top (Figure 1c). The sample can be annealed for a time t_R.
For the razor blade test, each of the two halves is floated on a thick polystyrene plate (2mm). After a first annealing, the plates are pressed against each other in order to form a 4-fold sandwich, during a time t_R (Figure 1d).
In both cases the interface can be studied as a function of the annealing time t_R.

Neutron reflectivity data (Figure 2)
They are obtained on the time-of-flight spectrometer EROS of LLB, for two angles θ (1.3° and 1.5°) with wavelengths in the range 4 Å to 25 Å. We take advantage of the difference in effective index between perdeuterated and non perdeuterated polymers. We have simulated the reflectivity by a profile of concentration in deuterated polymer, which is close to symmetric, by the error function from the classical laws of inter-diffusion. We give in Figure 2 the equilibrium widths σ, when the profile does not spread anymore with increasing annealing time, for the diffusion of polystyrene chains into a polystyrene network for N around 250.
In a first regime of low molecular weight M, the chains diffuse inside the network by more than their own size: $\sigma > R_g$. In the corresponding intermediate stages, we can measure the diffusion coefficients directly from the widening of the interface with time. We observe that the chains are noticeably slower than in a melt.
In a second regime of larger molecular weight, σ is lower than the global size of the chain ($\sigma < R_g$). The large chains do not penetrate completely because their entropy of mixing becomes too low to balance the elastic deformation energy due to their presence in the network. The limit size of the interface is close to that of a polymer strand between two cross-links (i.e. a piece of chain of N units).
Thus, by varying N or the molecular weight, we have the possibility of tuning at will the interfacial width, and to see its effect on adhesion between the layers.

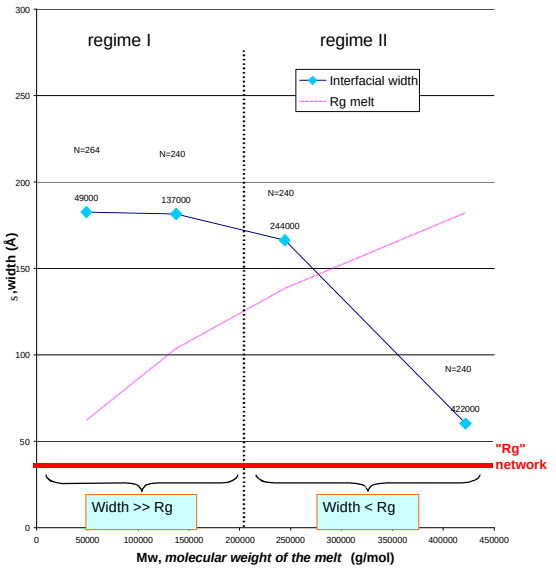

Figure 2. Neutron reflectivity data showing variation of the interfacial width s versus the molecular weight of the melt, M_w.

Razor blade test data (Figure 3, 4, 5).
In order to measure the adhesion energy, we insert a razor blade in the symmetry plane of the 4 fold sandwich, between the two polymer layers (Figure 3). The thick plates are here to store some elastic energy of bending, which will transfer into a plastic zone of deformation at the tip of the fracture. The distance **a** between the blade and the tip (measured after waiting 24 hours) gives the surface energy **G (J/m^2).**

Figure 3. Razor blade test

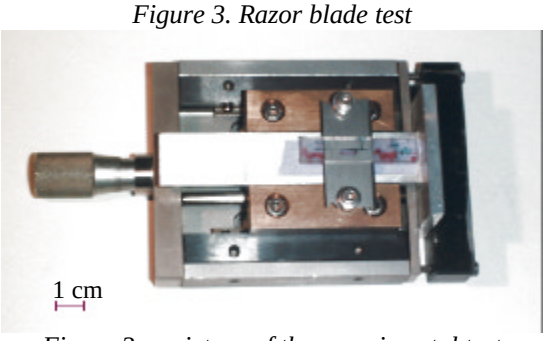

Figure 3a : picture of the experimental test

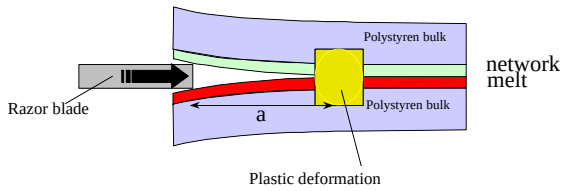

Figure 3b : diagram of test

After that the fracture has completely propagated, we can control by ion beam tests the amount of deuterium on both sides of the fracture. Thus we can check whether the fracture propagates between the perdeuterated and non-perdeuterated layers. We have also made microscopy observations of the tip zone (Figure 4**)**: the usual propagation is by a stick slip process: one has deviation with respect to the symmetry plane (an asymmetric mode called 2), until a new fracture restarts in the symmetry plane. One can also observe interference fringes ahead of the tip, in the craze region (polymer-specific cracks made of fibrils of chains).

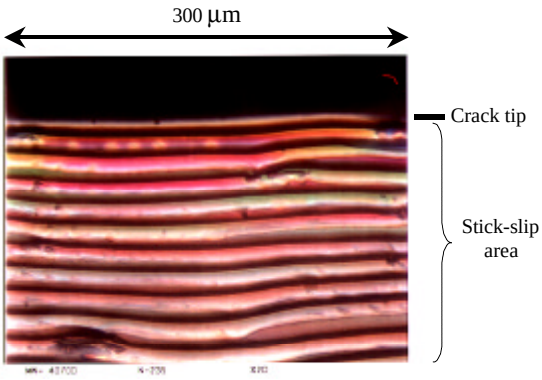

Figure 4. Top view of a crack sample made of a melt (Mw= 40700 g/mol) and a network (N=235 units between cross-links).

Figure 5 shows that in the molecular weight range I of Figure 2, the toughness **G** increases. This could be explained by the increasing degree of entanglement of a longer chain inside the network (indeed it is observed for two uncross-linked layers that **G** increases with s). Conversely, in regime II (R_g>σ), this effect should stop since the width s stops increasing. However, we see in Figure 5 that **G** keeps increasing. As an explanation, we only see at the moment the viscoelastic dissipation, which increases with molecular weight, or a kind of "knotting" of the long chains at the interface (see below).

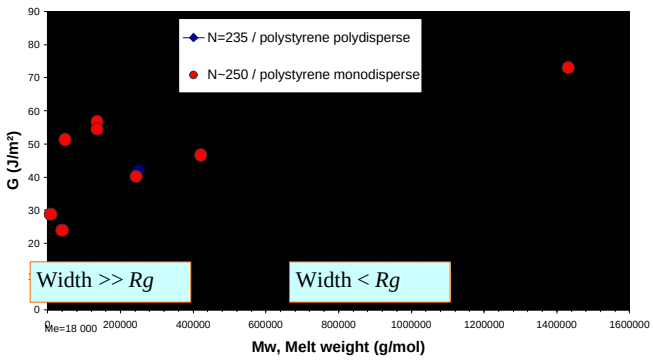

Figure 5. Plot of the toughness of the interface versus the molecular weight of the melt, M_w, static measurements

In summary, we are able to vary the interfacial width in some equilibrium conditions, which gives us a way to observe the influence of this width on the interfacial strength. It seems that the width is not the only driving parameter. Another one could be the configuration of the chains at the interface: a simplistic idea is the formation of loops by long chains in and back out of the network. We plan now to use different degrees of cross-linking in order to vary this configuration.